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A comment upon the aggregation of squaraine dyes

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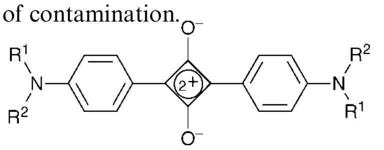
The electrospray ionisation mass spectrum (ESI-MS) of 2,4-bis[4-(*N*-methyl-*N*-butylamino)phenyl]squaraine shows peaks which correspond to the fragmentation pattern of the dimeric aggregate (*e.g.* $m/z = 810$ $[2M+2H]^+$) and, although the molecule is centrosymmetric, solid solutions of the dye exhibit second-harmonic generation (SHG). In order to satisfy the structural requirement the nonlinear optical behaviour is attributed to the dimeric aggregate which must be non-centrosymmetric. In contrast, solid solutions of the tetrahydroxy analogue, 2,4-bis[4-(*N*-methyl-*N*-butylamino)-2,6-dihydroxyphenyl]squaraine, are SHG-inactive and the ESI-MS data are consistent with the formation of a heptameric aggregate ($m/z = 819$ $[1.75M]^+ \equiv [7M]^{4+}$). The aggregation number is compound specific and an extensive study of fourteen anilino squaraines has shown direct correlation between the type of aggregate and the occurrence or absence of SHG.

Squaraine dyes have properties which may be applied to electrophotographic devices,[1] optical recording,[2] third-order nonlinear optics[3] and surprisingly, the frequency-doubling of light.[4] The donor–acceptor–donor structure is centric but, in spite of this, SHG has been observed from Langmuir–Blodgett (LB) films of a variety of analogues with anilino[4–7] and heterocyclic[8,9] donors. The SHG is not inherent to the molecule and, furthermore, the intensity is too strong to be associated with the glass|LB interface. Instead, it is attributed to the aggregate which must be non-centrosymmetric. It is assumed that the molecules adopt a T arrangement and that the SHG arises from intermolecular charge transfer between the acceptor and donor moieties. There is evidence that the squaraine aggregates persist in solution and that the properties are dependent upon the type of association and the extent of the intermolecular donor–acceptor interaction.[4,6] For example, Chen *et al.*[10] have reported the inclusion of anilino squaraines as monomers in aqueous solutions of β-cyclodextrin and as dimers in the larger cavity of γ-cyclodextrin, the absorption maximum being hypsochromically-shifted from 650 to 594 nm. McKerrow *et al.*[11] have observed two types of aggregate, J and H, by arrested crystallisation from dimethyl sulfoxide–water mixtures. Using a Bernesi–Hildebrand analysis, Chen *et al.*[12] have disclosed that the supramolecular unit of the anilino squaraine is tetrameric and has a cyclic chiral structure. Furthermore, Langley *et al.*[13] have reported that the electrospray mass spectra of the 2,4-bis[4-(*N*,*N*-dialkylamino)phenyl]squaraines (dye **1**) show aggregate peaks which may be assigned to $[nM+Na]^+$ where $2n$ is an integer and $4 \leqslant 2n \leqslant 9$. They have suggested that the sodiation is a 'true reflection of the behaviour of these species in solution' which, if correct, would have far reaching consequences on the control of the aggregation for commercially relevant applications. However, it is more likely that the sodiation is a consequence of contamination.



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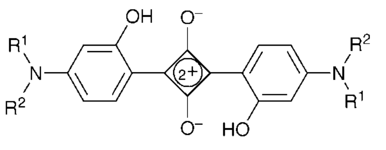

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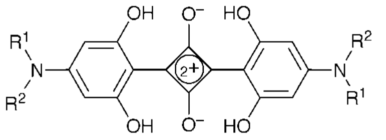

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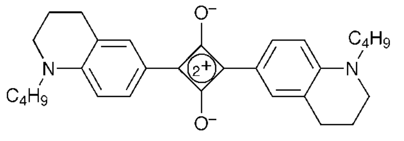

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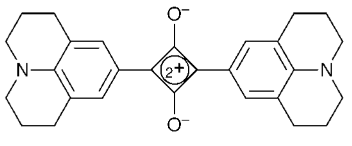

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In this work, the aggregation of dye **1** has been reinvestigated and, in addition, the electrospray mass spectra and nonlinear optical properties of several anilino squaraines are reported. The results of Langley *et al.*[13] have been reproduced by doping with Na^+ (or K^+ to give the potassiated species) but importantly, for solutions of the pure dye, none of the spectra shows evidence of metallation. Furthermore, the Cranfield ESI-MS data reveal m/z values which may be assigned to dimeric (or multiples of two for $z > 1$), hexameric and heptameric aggregates. The association number is compound specific and there is a direct correlation between the type of aggregate and the SHG activity for dyes **1** to **5**.

Experimental

Squaraine dyes were synthesised using published procedures[14] and characterised by ^1H NMR, elemental analysis and ESI-MS. A VG Quattro quadrupole mass spectrometer (upgraded to Quattro II specifications) and MassLynx data system (VG Organic, Altrincham) were used in the positive ion electrospray mass spectrometry study at the Michael Barber Centre (UMIST). Experiments were performed with the electrospray source high-voltage lens at 0.32 kV and the source sampling cone voltage at 25 V. Electrospray data were collected in the mass range m/z 100–2500 for dilute solutions of the dye (10 $\mu g\ cm^{-3}$) in (*a*) CH_3CN, (*b*) a 4 : 1 mixture of CH_3CN–H_2O

and (*c*) a 4 : 1 mixture of CH_3CN–H_2O containing 0.1% formic acid. The spectra were averaged over 15 scans with a scan rate of 100 amu s^{-1} and a flow rate of 5 µl min^{-1}. The spectrometer was calibrated using polyethylene glycol.

Spun-coated films were obtained by spreading *ca.* 500 µl of a dilute chloroform solution of the dye and poly(vinyl acetate) onto a glass substrate and rotating the substrate at 500 rpm using a Headway spin-coater. SHG measurements were performed in transmission with the p-polarised laser beam (Nd : YAG, $\lambda = 1064$ nm) at an angle of 45° to the film.

Results and Discussion

Structure–property relationship

LB films of the anilino squaraines exhibit strong SHG[4–9] and the second-order properties result from the aggregate structure which must be non-centrosymmetric and not from the centric molecule itself. Spun-coated films of some but not all of the squaraines in poly(vinyl acetate) are also SHG-active. The second-harmonic intensity increases with the concentration of dye but is weak in comparison with the signal from the LB monolayer. Nonetheless, its observation corroborates the persistence of the aggregates in solid solution and the non-centrosymmetry, necessary for second-order effects, probably results from a partial orientation of the acentric species in the spinning process. The SHG-active films include several alkyl analogues of the anilino squaraine (**1b**–**1g**), the dihydroxy substituted derivatives (**2a**–**2c**), and the heterocyclic analogues (**4** and **5**). A common feature of their electrospray mass spectra is a high mass peak, or fragmentation pattern, which may be assigned to the dimeric aggregate (Fig. 1–3).

An assignment of the *m*/*z* values for 2,4-bis[4-(*N*-methyl-*N*-hexylamino)phenyl]squaraine (dye **1c**: $R^1 = CH_3$, $R^2 = C_6H_{13}$) is given in the legend to Fig. 1. The monomeric species is observed as a dihydrogenated ion ($m/z = 462$, $[M + 2H]^+$), this being previously reported by Law and co-workers[15] for other anilino squaraines. Furthermore, a peak corresponding to the trihydrogenated dimeric aggregate ($m/z = 923$ $[2M + 3H]^+$) is shown and the main fragmentation results from the progressive loss of one to four $(CH_2)_5$ units. The *N*-methyl-*N*-butylamino to *N*-methyl-*N*-decylamino analogues of dye **1** also form dimeric aggregates (Table 1) but for the higher analogues, dodecyl to docosyl, fragmentation of the alkyl groups makes it difficult to unambiguously assign the MS data. In contrast, the spectra of the heterocyclic analogues (**4** and **5**) show a single high mass peak which may be assigned to $[2M + nH]^+$ (Fig. 2 and 3).

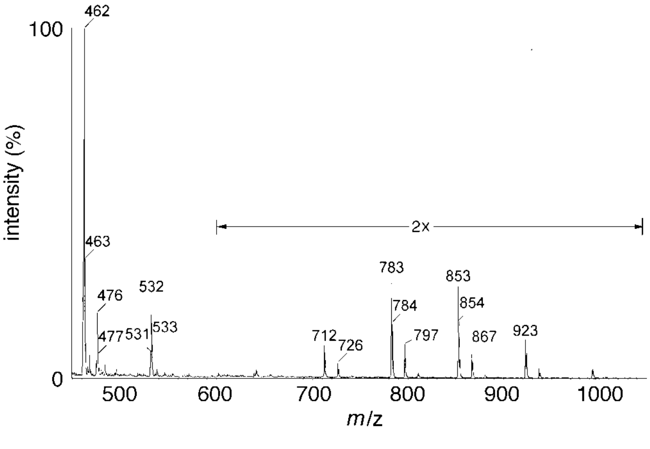

Fig. 1 Electrospray mass spectrum of 2,4-bis[4-(*N*-methyl-*N*-hexylamino)phenyl]squaraine **1c**. Monomer: $m/z = 462$ $[M + 2H]^+$. Aggregate: $m/z = 923$ $[2M + 3H]^+$; 867 $[2M + 3H - 4CH_2]^+$; 853 $[2M + 3H - 5CH_2]^+$; 797 $[2M + 3H - 9CH_2]^+$; 783 $[2M + 3H - 10CH_2]^+$; 726 $[2M + 2H - 14CH_2]^+$; 712 $[2M + 2H - 15CH_2]^+$.

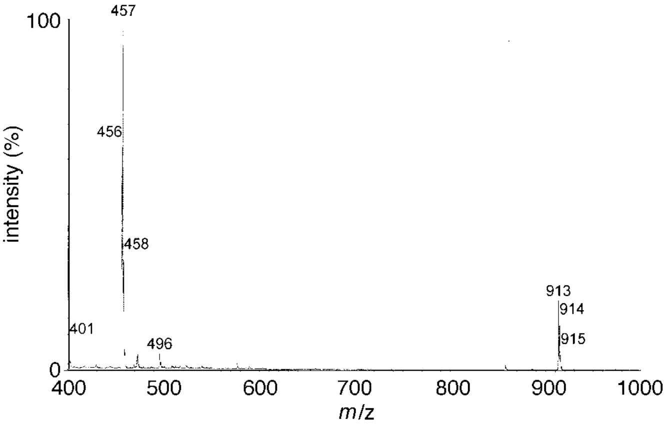

Fig. 2 Electrospray mass spectrum of 2,4-bis[6-(*N*-butyl-2,3,4-trihydroquinoloyl)]squaraine **4**. Monomer: $m/z = 457$ $[M + H]^+$. Aggregate: $m/z = 913$ $[2M + H]^+$.

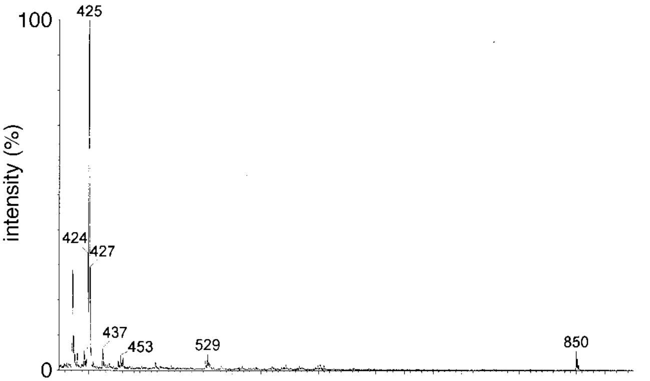

Fig. 3 Electrospray mass spectrum of 2,4-bis(9-julolidinyl)squaraine **5**. Monomer: $m/z = 425$ $[M + H]^+$. Aggregate: $m/z = 850$ $[2M + 2H]^+$.

Table 1 Positive ion electrospray MS data[a]

dye	amino group R^1–N–R^2	RMM	aggregates (*m*/*z*) $[1.5M]^+$	$[1.75M]^+$	$[2M + nH]^+$
1a	CH_3–N–CH_3	320	480	—	—
1b	CH_3–N–C_4H_9	404	—	—	811
1c	CH_3–N–C_6H_{13}	460	—	—	923
1d	CH_3–N–C_8H_{17}	516	—	—	1033
1e	CH_3–N–$C_{10}H_{21}$	572	—	—	1146
1f	C_4H_9–N–C_4H_9	488	—	—	977
1g	C_5H_{11}–N–C_5H_{11}	544	—	—	1089
2a	CH_3–N–CH_3	352	528	—	—
2b	CH_3–N–C_4H_9	436	—	—	873
2c	C_4H_9–N–C_4H_9	520	—	—	1041
3a	CH_3–N–C_4H_9	468	702	819	—
3b	CH_3–N–C_6H_{13}	524	786	917	—
4	—	456	—	—	913
5	—	424	—	—	850

[a] None of the ESI-MS spectra showed significant peaks at *m*/*z* values greater than those listed.

The tetrahydroxy substituted squaraines, 2,4-bis[4-(*N*-methyl-*N*-alkylamino)-2,6-dihydroxyphenyl]squaraine (**3**), differ in so far as their solid solutions do not exhibit SHG and the electrospray spectra show aggregate peaks which correspond to fractional values of the relative molecular mass: *e.g.* $m/z = 702$ and 786 $[1.5M]^+$ and 819 and 917 $[1.75M]^+$ respectively for the butyl and hexyl analogues (see Fig. 4). The former may be assigned to the trimeric aggregate if $z = 2$. Alternatively, the peaks may be attributed to hexameric and heptameric species respectively if $z = 4$ and, although they may

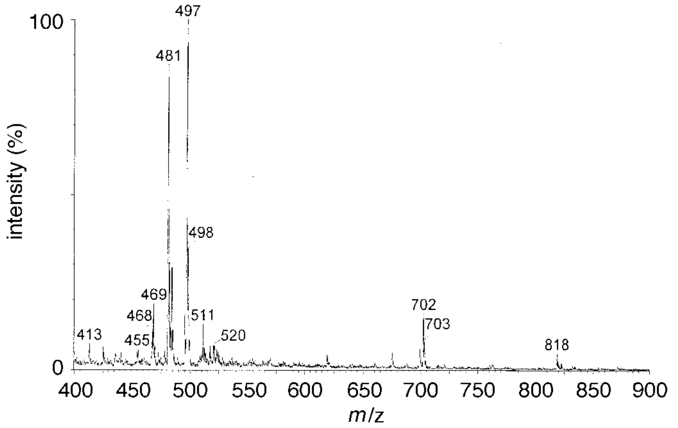

Fig. 4 Electrospray mass spectrum of 2,4-bis[4-(*N*-methyl-*N*-butylamino)-2,6-dihydroxyphenyl]squaraine **3a**. Monomer: $m/z=469$ $[\mathrm{M+H}]^+$. Aggregate: $m/z=819$ $[1.75\ \mathrm{M}]^+ \equiv [7\mathrm{M}]^{4+}$; 702 $[1.5\mathrm{M}]^+ \equiv [6\mathrm{M}]^{4+}$. The peak at 818 $[1.75\mathrm{M}-\mathrm{H}]^+$ is stronger and has been labelled instead of 819.

exist as separate entities, the lower aggregate may result from the fragmentation of the heptamer. Furthermore, Chen *et al.*[12] have previously suggested the formation of a cyclic tetrameric aggregate and, thus, it is feasible that the molecules of the heptameric aggregate adopt a bicyclic arrangement in which two tetramers are fused.

The ESI-MS data for the *N*,*N*-dimethylamino analogues of **1** and **2** also correspond to fractional values of the aggregate mass ($m/z=480$ for **1a** and 528 for **2a**, $[1.5\mathrm{M}]^+$). The fragmentation patterns are similar and may be assigned to the progressive loss of the CH_2 and amino groups and, for the dihydroxy derivative, the loss of both oxygens (Fig. 5; Table 2). Close scrutiny of the spectra suggests that the dyes probably form the hexameric aggregate ($[1.5\mathrm{M}]^+ \equiv [6\mathrm{M}]^{4+}$) rather than the trimeric species ($[1.5\mathrm{M}]^+ \equiv [3\mathrm{M}]^{2+}$), the peaks at *ca.* 455.5 corresponding to the loss of $7CH_2$ for $z=4$ and a non-integral number for $z=2$. Furthermore, solid solutions of these dyes are SHG-inactive and it is assumed that the aggregate structure is centrosymmetric. In fact, none of the materials with *m*/*z* values corresponding to fractional values of the relative molecular mass, *i.e.* $[1.5\mathrm{M}]^+$ or $[1.75\mathrm{M}]^+$, have thus far exhibited SHG when deposited as spun-coated solid solutions.

Table 2 Assignment of the aggregate fragmentation patterns of 2,4-bis[4-(*N*,*N*-dimethylamino)phenyl]squaraine (**1a**) and 2,4-bis[4-(*N*,*N*-dimethylamino)-2-hydroxyphenyl]squaraine (**2a**)

ESI-MS data (*m*/*z*) **1a**	**2a**	possible assignment[a]	mass (*m*/*z*)
—	528	$[6\mathrm{M}]^{4+}$	528
480	—	$[6\mathrm{M}]^{4+}$	480
456	455	$[6\mathrm{M}-7\mathrm{CH_2}]^{4+}$	455.5
438	439	$[6\mathrm{M}-12\mathrm{CH_2}]^{4+}$	438
424	—	$[6\mathrm{M}-16\mathrm{CH_2}]^{4+}$	424
415	414	$[6\mathrm{M}-6\mathrm{D}]^{4+}$	414
402	403	$[6\mathrm{M}-22\mathrm{CH_2}-7\mathrm{D}]^{4+}$	403
392	393	$[6\mathrm{M}-8\mathrm{D}]^{4+}$	392
370	368	$[6\mathrm{M}-10\mathrm{D}]^{4+}$	370

[a] The two dyes show almost identical fragmentation patterns and, for simplicity, the listed MS fragments are for **1a**; the fragments of dye **2a** also exclude the oxygen atoms of the hydroxy groups. $\mathrm{D}=-\mathrm{N(CH_3)_2}$ (donor).

The solution spectra of these dyes typically display an intense monomer peak at *ca.* 635–665 nm with half widths at half maximum of 7–13 nm and, additionally, a broad shoulder which may be assigned to the aggregate. It is not possible to relate the nonlinear optical behaviour to the spectra because the monomer absorption, albeit sharp, masks that of the less abundant aggregate. However, using the method of McKerrow *et al.*,[11] arrested crystallisation from solution has provided absorption maxima at *ca.* 650–700 nm for the SHG-active dyes, those which form dimeric aggregates, with the maxima being hypsochromically shifted to 530–550 nm for the inactive species, the hexameric and heptameric aggregates. Furthermore, correlation between the linear and nonlinear optical properties and the aggregate structures of anilino squaraines has been established for LB films.[4–7] Significantly, transitions involving a hypsochromic shift of the LB absorption band invariably result in the loss of SHG[6] and, typically, the SHG-inactive phase is associated with a narrow absorption at *ca.* 530 nm and no significant higher wavelength shoulder. The molecules probably adopt a parallel face-to-face arrangement whereas, for the SHG-active LB films and solution aggregates, the structural requirement can only be met if there is non-parallel alignment. It is therefore assumed that the molecules of the dimeric aggregate adopt a T arrangement with intermolecular charge transfer between the donor (anilino) and acceptor (C_4O_2) moieties. This was suggested in a previous report[4] and the hypothesis has since been corroborated by the theoretical analysis of Brédas and Brouyère.[16]

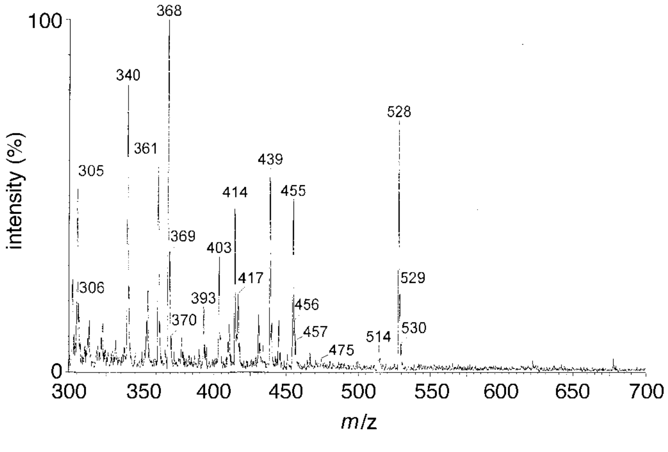

Fig. 5 Electrospray mass spectrum of 2,4-bis[4-(*N*,*N*-dimethylamino)-2-hydroxyphenyl]squaraine **2a**. Monomer: $m/z=353$ $[\mathrm{M+H}]^+$. Aggregate: $m/z=528$ $[1.5\mathrm{M}]^+ \equiv [3\mathrm{M}]^{2+}$ or $[6\mathrm{M}]^{4+}$.

Effect of doping with Na^+ and K^+

Langley *et al.*[13] reported ESI-MS data for three of the anilino squaraines listed in Table 1 (labelled **1b**, **1f** and **1g**) and assigned the aggregate peaks to $[n\mathrm{M}+\mathrm{Na}]^+$ where $2n$ is an integer and $4 \leqslant 2n \leqslant 9$. They proposed that the sodiation is a true reflection of the aggregates in solution whereas, in this work, the ESI-MS data for dye **1** and several related squaraines clearly show that it is not. However, the metallated species may be obtained by doping with NaBr (or KBr to give the potassiated aggregate). The results are listed in Table 3 and, interestingly, the fine structure of the fragmentation pattern of

Table 3 ESI-MS data of undoped and lightly doped samples of 2,4-bis[4-(*N*-methyl-*N*-alkylamino)phenyl]squaraine where the alkyl group is butyl (dye **1b**) and hexyl (dye **1c**)

	undoped (*m*/*z*)		Na^+ doped (*m*/*z*)		K^+ doped (*m*/*z*)	
assignment[a]	**1b**	**1c**	**1b**	**1c**	**1b**	**1c**
monomer						
$[\mathrm{M}+2\mathrm{H}]^+$	406	462	406	462	406	462
$[\mathrm{M}+\mathrm{H}+\mathrm{A}]^+$	—	—	428	484	444	500
aggregate						
$[2\mathrm{M}+3\mathrm{H}]^+$	810	923	811	923	811	923
$[2\mathrm{M}+2\mathrm{H}+\mathrm{A}]^+$	—	—	833	945	849	962

[a] A = alkali metal (Na^+ or K^+). Higher aggregates of general formula $[x\mathrm{M}+y\mathrm{H}+z\mathrm{A}]^+$ have been observed but their occurrence is dependent upon the concentration of dopant.

2,4-bis[4-(*N*-methyl-*N*-hexylamino)phenyl]squaraine is mimicked by the sodiated and potassiated peaks with the *m*/*z* values being shifted by 22 and 38 respectively. It is relevant that Langley *et al.*[13] used a mixture of NaI and CsI as the calibrant and this is a likely source of contamination of their ESI-MS data. The results of this study clearly indicate that the aggregates freely exist, even in dilute solution, and their presence is manifested by the second-order properties.

Conclusion

Squaraine dyes associate in solution and the ESI-MS analysis has revealed *m*/*z* values which may be assigned to acentric dimeric aggregates (or multiples of two if $z > 1$) which are SHG-active and to hexameric and/or heptameric aggregates which are not. The aggregation number is compound specific and, for the anilino squaraines, the higher aggregates may be obtained by using hydroxy substituents and less sterically hindered *N*,*N*-dialkylamino groups. It is assumed that hydrogen bonding and chromophore-dominated interactions play an important role in determining the aggregate structure.

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